

SONOCHEMICAL TREATMENT OF FUEL COMPONENTS

Kazem M. Sadeghi, Jiunn-Ren Lin, and Teh Fu Yen
Department of Civil and Environmental Engineering
University of Southern California
Los Angeles, CA 90089-2531

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ABSTRACT

A new method has been developed to recover upgraded lighter-hydrocarbon liquid oil from an asphaltene-containing oil material (tar sand, asphalt, heavy oil, shale oil, coal liquids, etc.). The process follows of dispersing particle of the carbonaceous material in an aqueous solution containing inorganic base (NaOH, Na_2SiO_3 , etc.) and/or surfactant at ambient temperatures and pressures. With the aid of sonication energy, the inorganic base and/or surfactant will combine with the polar components of the fuel to speed the recovery of upgraded oil material. The reaction process essentially removes and/or converts the asphaltene fraction in the bituminous material to lighter fractions. The process is highly efficient and the reaction time in minutes for the samples examined. The reaction mechanisms are related to principles of sonochemistry as well as membrane mimetic chemistry.

INTRODUCTION

The time has come for a new chemical process to improve the old refining technology that has not been revolutionized over a century. The new process has been developed and proved to recover upgraded lighter fuels from asphaltene-containing oil compounds. The writers have studied membrane mimetic chemistry and have applied the principles to sonochemistry.^{1,4,9} In most of the material studied, self-inducing, in-situ surfactants are generated or an external surfactant is introduced to initiate the process of upgrading.

The reactions initiated by ultrasonic irradiation in this country began 50 years ago.¹⁴ Since then, the mechanism of acoustic chemical reactions had remained poorly understood, thus limiting its practical application. Yet, in recent years, some considerable advances have been made in the technological generation of newer, higher intensity ultrasonic generators. Advances in ultrasonic waves are also becoming more successful in enhancing chemical processing operations by increasing the rates of individual transport phenomena involved in the overall operation.

In recent years, this problem has been reexamined, especially that part involving the application of cavitation in a microenvironment. For example, in aqueous solution, the instantaneous pressure at the center of a collapsing bubble has been estimated from theoretical considerations to be about 75,000 psi (5,100 atm).¹⁰ Experimentally, cavitation thresholds up to 300 bars (3.0×10^7 Pa) have been obtained.¹⁵ The actual cavitation temperature has been similarly measured as high as 5200 ± 560 K.³ The industry is therefore slowly being awakened to this powerfully unique manner and feasibility for large scale processes.

This new process developed by the writers^{5,19,20} operates at ambient temperature and atmospheric pressure. The hydrogen supply is either from the water or a stream of hydrogen bubbles. The recovered upgraded fuel is lower in heterocyclic elements content and metals can be recovered. This reduces process cost and minimizes adverse environmental impact. The fuel samples used are tar sand, asphalt, heavy oil, coal liquids and even oil shales.

EXPERIMENTAL AND RESULTS

Tar Sands

The sample used is high grade Athabasca tar sand, from McMurray Formation. The Kentucky tar sand from Edmonson Formation as well as the California tar sand from Sisquoc Formation have also been investigated.¹⁸ In the case of tar sand both separation as well as upgrading are achieved. The methodology calls for an alkaline solution with the aid of sonication. Stirring is applied only to help mix the solution with the sample and is not a major factor in the extraction. Usually, two different alkalis were used to extract

the bitumen: (1) 20:1 by volume distilled water to sodium silicate [wt. ratio $\text{SiO}_2/\text{Na}_2\text{O} = 1.80$] (PQ Corporation) and (2) 0.02 M NaOH (J.T. Baker Chemical Co.) solution. The stirrer operates at 320 rpm with the blade at 2 cm above the sample. Sonication was performed in a 10-gallon 40 kHz transducerized tank (Branson model EMA30-6). Six piezoelectric transducers, made from lead zirconate titanate ceramic, were bonded to an area of about 350 cm^2 directly at the bottom of the tank. The six transducers consume a total power of 180 W/cm^2 and deliver approximately 2.0 W/cm^2 acoustic intensity at the transducer surface. Ultrasonic energy is directed upward through the tank. A typical example is that 200 g of tar sand are applied to 1000 mL of alkaline solution and sonicated for 20 minutes with the addition of few drops of 30% hydrogen peroxide as free-radical initiators. The solution temperature is observed at 45°C . The bitumen is skimmed from the surface solution at intervals and oven dried overnight under a vacuum at 50°C . For the upgraded bitumen, an average gravity of 15° API is found, based on a 95% cumulative recovery (see Figure 1, circles 1-6). The bitumen from Athabasca sample has an average value of 8° API in its raw state. Agglomerates are the heavier asphaltenes and preasphaltenes that couple with the metals (Ti, V, etc.) to form a charcoal-like materials that precipitate (ca. 5%) to the bottom (circle 7, Figure 1). The microemulsion of micelles to form surfactants have been reported previously to be stable for many years.⁶ Figure 1 is a plot of the heterocyclic elements content X, $X = \text{S} + \text{N} + \text{O}$ versus the hydrogen enrichment, while all the elements are in atom basis. In the same figure the solvent fractionation products from the raw tar sand bitumen are also located. This indicates a positive upgrading in quantitative recovery. Material balance on the hydrogen content cannot account for the interconversion of the products from this new process alone. The extra amount of hydrogen must be derived from the water.

Asphalt

Regular paving asphalts obtained through the material bank of the Strategic Highway Research Program (SHRP) are used for the investigation.²² To isolate the asphaltene fraction, Soxhlet extractor is used with n-pentane as the eluent for more than 24 h. The n-pentane insoluble fraction is dried overnight in vacuum and used as asphaltene in this work. For each run, 0.50 g of asphaltene is dissolved in 1.0 g toluene and 30 g of water is added gradually to a 50 ml flask. To increase the interfacial surface area, vigorous stirring during the water addition is employed to form an oil in water emulsion. Model VC-500 ultrasonic processor (Sonics & Materials, Inc.) at power level 10 kW is used in the process. Instead of hydrogen gas a reducing agent, sodium borohydride, is introduced and hydrogen bubbles are evaluated. Span 20 is commonly employed as extra surfactant for the conversion reaction. After the reaction, the asphalt constituent is extracted by the dichloromethane. Both 30 mL of dichloromethane and the sample after reaction are put into the separation funnel and shaken several times. Two layers will appear in a short time. Since part of the emulsion is quite stable and hard to extract from the oil phase, shaking several times is generally required at that point. Since analysis of the asphalt content is dependent on the four fraction ratios, part of the product remaining in the water phase will not affect the analysis result. the dichloromethane with asphalt will stay in the bottom layer. After 10 minutes, the bottom layer in the separation funnel is collected for further analysis.

The composition of asphalt sample is determined through the TLC/FID analysis in this study. Before starting the analysis, a blank scan of Chromarod is required to ensure the removal of contaminants. Around 1 μL of sample is spotted on the Chromarod-SIII which is made by Iatron Laboratories, Inc. Since humidity will significantly effect the result of TLC development and reproducibility tremendously, preserving the Chromarod in the constant humidity chamber for at least 10 minutes to reach equilibrium is necessary. The constant humidity chamber is a chamber with sulfuric acid inside. Thus, the relative humidity will stay at 25% while reaching equilibrium. Two solvents with different polarities, including toluene and a mixture of dichloromethane and methanol at a ration of 95 to 5, are used to developed the sample into three fractions. The oil fraction will expanded first in the TLC development chamber by using toluene as an eluent. Using the mixture of dichloromethane and methanol as an eluent will expand the resin fraction. Since the asphaltene fraction is mostly polar, it will stay in the same spot. After development, the Chromarod is mounted on the rack and the analysis is run in the Itatrosan TH-10 analyst. Hydrogen pressure and air flow rate used for FID analysis are 0.9 in Hg and 2000 cfm, respectively. The HP 3390A integrator is connected to obtain the composition for three different fractions. Data are collected within 1 minute for each sample. The result of a typical experiment is shown in Figure 2 where various concentration of Span 20 is used. Evidently the decrease of asphaltene concentration as well as the accompanied increase of resin and gas oil

content suggest that upgrading can be accomplished in a reasonable time (time used is 15 minutes). Other types of extra-aided surfactant also has been investigated.

Heavy Oil

A California Monterey native crude oil (18°API, Well Blockmen #1) after vacuum dewatering and evaporation of light fraction obtained was used in the study. This topped crude contains 68.3% of resin and oil, 29.7% of asphaltene, and 2.0% of preasphaltene (carbene and carboid). For each run heavy oil upgrading study, 9.0 g of heavy crude is mixed with 10 mL of toluene and 250 mL of 10% aqueous sodium silicate solution. The mixture is placed into 1 L three necked-round bottom flask equipped with a mechanical stirrer and water cooling condenser. The reactor is placed in a water bath at 55°C in the Branson's ultrasonic unit with six piezoelectric transducers as described in Tar Sand Section. Sonication is continuously applied to the system for 5 to 10 hours. During the reaction, 2 mL of hydrogen peroxide is applied into the reactor. After sonication, the solution is poured into a separation funnel and the crude product was extracted by dichloromethane. The organic phase and aqueous phase separate within 5 minutes. The organic phase is subjected to vacuum evaporation to remove the dichloromethane from organic phase. The 1 L of n-pentane is added to the crude products to make sure the precipitation of asphaltene fraction. Asphaltene fraction is determined after filtration and drying in a vacuum oven. The quantity of oil and resin fraction is determined after the removal of n-pentane by vacuum evaporation. The toluene insoluble fraction is termed preasphaltene.

Figure 3 summarizes all the separate experiments and evidently the asphaltene has converted into oil and resin. After reaction, the oil and resin fraction content increases from 68.3% up to 86.0% and asphaltene content reduces from 29.7% down to 15.6%. From the mass balance, the recovery ranges 98% to 102%. Structural parameter such as H_A/H_S (from 1H NMR) and H_{MC}/H_S (from FT-IR) for the products have been supported the upgrading.⁴

Coal Liquid

The sample employed here is from a chromatography-separated fraction (benzene-eluent) of asphaltene isolated from the coal liquid by catalytic Inc. (Willsonville, AL) from the solvent refined coal process. the coal is from Bellicap Seam, a Wyoming sub-bituminous type. For each run, a 0.2 g of sample is used dissolved in 0.4 g of toluene. The asphaltene solution is mixed with 30 mL of spent sodium silicate solution (recovered from Tar Sand Experiment Section). For every 15 mL of sonication a quantity of 0.3 g of sodium borohydride is added for maintaining a constant hydrogen bubbling activities. The results are summarized in Figure 4.

From the results shown in the Figure 4, the coal asphaltene content reduces tremendously within a short reaction time. Within 60 minutes, the asphaltene content reduced to 45.2%. At the same time, the oil and resin content increased up to 54.8%. From chemical kinetics, it is seen that the reaction is significant within a short time.

Oil Shale

For oil shale, the process has modified¹⁶⁻¹⁷ to a simultaneous use of electrolytic oxidation and ultrasonic radiation in alkaline environment; up to 57% by weight of the oil shale system has been dissociated and suspended in a process solution. The oil shale sample used are Stuart oil shale (Brick Kiln Member, Queensland, Australia) and Maoming oil shale (leave shale outcrop deposits, Guangdong, China). On the basis of analytical results, the Brick Kiln member of Stuart oil shale contains approximately 19.0% (by weight) kerogen, less than 0.1% bitumen, 6.6% moisture, 3.3% combined water, and a residual mineral, mostly quartz and clays. Maoming oil shale contains approximately 25.5% kerogen, 1.25% bitumen, 1.2% moisture and 63% minerals dominant in kaolinite associated with montmorillonite interstratified with illite and amesite. Bitumen in the oil shale is extracted by using benzene/methanol (with a volume ration of 3/2) in a Soxhlet extractor for 72 h. The solvent-free bitumen is obtained after filtration and following vacuum evaporation procedures. Usually, electrolytic oxidation of oil shale is carried out by using a glass cell of 700 mL total capacity. The anode and cathode compartments are separated by a porous frit. The anode electrode is made of 50-mesh platinum gauze (3.2 X 5.0 cm²). A constant potential of 0.3 V was maintained throughout the oxidation. An ultrasonic transducer of 40 kHz (nominal) and about 60 W is mounted on the bottom of the electrolytic glass cell. Shale samples are ground to sizes between 40 and 100 mesh screen and

placed in the anode chamber together with a total of 500 mL of 3 N sodium hydroxide solution. The same solution is used in the cathode chamber. The mixture in the anode chamber is acidified with HCl to yield an precipitate. An enrichment of organic matter is found in the acid precipitate from the process solution where it contains more than 23% organic matter. The remaining residue oil shale contains only less than 12% organic matter. Therefore the enrichment of organic matter in the precipitate as well as in the process solution is evident. Furthermore, the kerogen structure is destroyed in this mild dissociation process. This is proven by using a bitumen-free shale sample, where carboxylic acids are formed by infrared (Nicolet's FT-IR) and identified by GC (Hewlett-Packard 5880A) after esterification of the process solution. The 1575 cm^{-1} represent in the organic matter recovered from dissociation process and the absence of the absorption band in kerogen and bitumen reflect that the organic matter as well as mineral aggregates have been transformed (Figure 5).

DISCUSSION

Process Mechanism

This process is unique in separating oil into upgraded asphaltene-free fractions low in metal content. Experimental results indicate that the separation process operates by the reaction of specific chemical components of the bitumen with alkaline solution (e.g., sodium hydroxide) in the presence of sonication. The in-situ surfactants formed thus to facilitate the bitumen separation by a membrane-mimetic mechanism.^{2,11} Both asphaltenes and resins consist of aromatic sheets with saturated and polar functional groups spaced closely on long chains. Asphaltenes in their natural state exist in micelle form, peptized with resin molecules.¹² The center of this micelle can be either metal (V, Ni, Fe, etc.) or silica (or clay), or trace water. The crucial feature is that the polar groups are concentrated towards the center. This is often called oil external-water internal or reversed micelle. Surface adhesion is mainly due to hydrogen bonding, although other intermediate bonding mechanism such as charge transfer and acid-base salt formation do exist.

Ultrasound induced cavitation causes emulsification of the asphaltene and resin molecules and reorganization of metal, polar, and non-polar components into a continuous, single phase micelle of the polar external form. The surfactants interact with resin molecules in a membrane-mimetic fashion²; that is, a selective cation (e.g., hydroxide or silicate) is activated and dissolved in the oil phase. In this manner, the molecule containing the heterocycle center is dissociated and any ionizable proton such as in COOH, SH, or NH is replaced with the cation. When the surfactant migrates into the micelle it disrupts the polar structure, forming a Hartley micelle or polar-external micelle, and consequently a gel or liquid crystal phase of vesicles may also form. The outer counter anions emulsify the oil, and the micellar structure becomes a micro-emulsion stabilized by the reagent molecules. Sonication contributes to the removal of the heteroatoms by decreasing hydrogen bonding and inducing charge transfer and salt formation, thus lowering viscosity and specific gravity and increasing and facilitating recovery of the bitumen.

Ultrasound Phenomena

The mechanisms responsible for the observed increases in transport rates and unit operation processes utilizing ultrasonic energy can be divided into two categories: (1) first-order effects of fluid particles (displacement, velocity, and acceleration); and (2) second-order phenomena (radiation pressure, cavitation, acoustic streaming, and interfacial instabilities). Usually, one or more of the second-order effects are responsible for the enhancements in the transport process.^{10,14} The ultrasonic vibration raises the solution temperature to 45°C,¹⁰ but the temperature rise has little effect on bitumen recovery.⁸ In fact, Ibishi and Brown¹³ reported a monotonic decrease in sonochemical yield with increasing temperature. Because ultrasound in both aqueous and organic media produces radicals, conventional free radical propagation, inhibition, termination occurs. Cracking of asphaltene based on Rice mechanism of pyrolysis also occurs.^{21,22}

Interfacial Hydrogenation

In some special fuels system such as oil shale the system need further operations such as swelling bonification or additional electrolytic oxidation. An interfacial reaction can enhance chemical reaction by generation of continuous renewable surfaces. The size of the microemulsion also can be controlled by the multilamellar-unilamellar vesicle formation. The fact the collision probability can be increased by 10^4 fold

by using a membrane-mimetic agent in micellar cage is naturally of advantage. In many cases the bubble size of evolved hydrogen gas or processing hydrogen gas can also be mediated.

CONCLUSIONS

Experimental results from a wide variety of fuel sources, coal liquids, tar sands, oil shale, asphalt and heavy oils all indicate that this new upgrading technology is feasible. The remaining development work leading to any useful industrial operations still need to be followed and completed. Upon completion of development work, a second generation refining technology may be born with the minimum environmental impact since this new process can be conducted at room temperature and ambient atmosphere and all the process can be made in modules with enclosed pathways.

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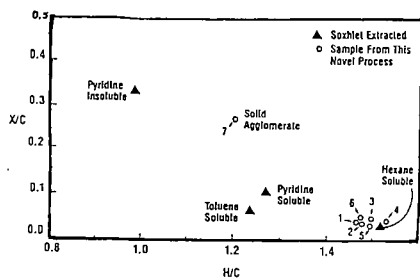


Figure 1. X/C versus H/C for various fractions of bitumen from Athabasca tar sand. Circles 1 through 6 are the recovered bitumen from the surface of solution and circle 7 is the solid agglomerate precipitate. Soxhlet extraction of the raw bitumen as reference points.

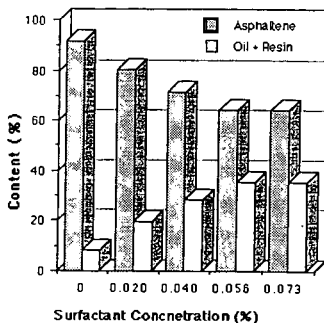


Figure 2. The conversion of asphaltene to oil and resin at various surfactant content (reaction time : 15 minutes). The asphaltene is isolated from a paving asphalt (AAX). The surfactant is Span 20.

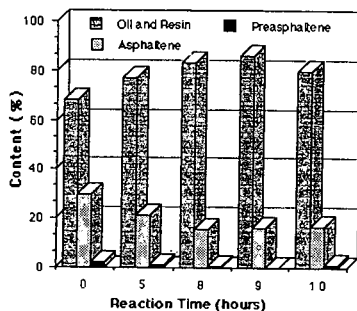


Figure 3. The composition of a Monterey native crude oil at various reaction time after sonication process. Each time interval represents a separate experiment.

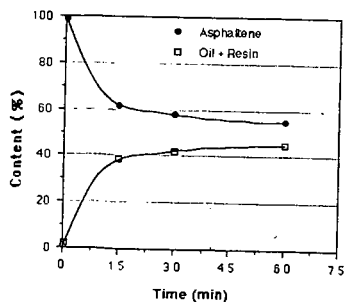


Figure 4. Conversion of a coal-derived asphaltene fraction from coal liquid with time. The sample is isolated from Catalytic Inc. at Wilkesville, AL.

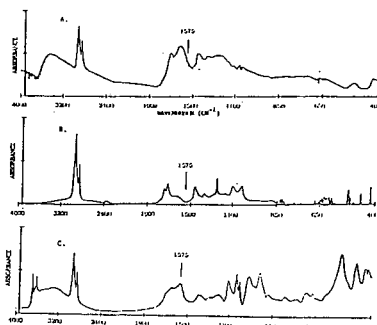


Figure 5. FT-IR spectra of a Maoming oil shale (A) isolated kerogen in KBr, (B) raw bitumen in CCl_4 , and (C) organic matter recovered from dissociation process. The 1735 cm^{-1} represent carboxylic acids.